

REMARKS

Claims 1- 16 are pending and stand rejected.

Response to the Examiner's "Response to Arguments"

In response to Applicant's remarks that the Akio reference fails to teach or suggest alkoxyamines, the Examiner mentions that while the Akio reference does not explicitly show the structure of core (I), it discloses a similar inorganic radical with molecular mass of greater than 14, and therefore it would have been obvious for the core (I) to have a similar structure to Ia or Ib.

Applicant respectfully disagrees. The structures of core (I) result from the thermal decomposition of the corresponding alkoxyamines – from a nitroxide controlled radical polymerization process. The Akio reference teaches obtaining block copolymers by an Atom Transfer Radical Polymerization (ATRP) technique, that does not result in Applicant's claimed alkoxyamine residuals as the core. There is a big difference in the two controlled radical polymerization techniques. Not only is the residue of the different control agent different, but there ATRP process involves catalysis with copper complexes to synthesis the block copolymers. Unfortunately the copper complexes from the ATRP process are highly colored molecules that reduce the transparency of the resultant films. Applicant's claimed films do not have the color problems of block copolymers formed by the Akio ATRP process.

The Akio films are not the same or similar to Applicant's films, due in part to the CRP process used, and the connected color issue of the Akio ATRP process.

35 U.S.C. §103(a)

Claim 1-15 stand rejected under 35 U.S.C. §103(a) as being unpatentable over Akio et al (JP 2002194167 machine translation). The JP '167 reference describes a blend of a core-shell modified acrylic resin and an acrylic/methacrylic block copolymer. The block copolymer is formed by a atom transfer radical polymerization (ATRP) involving a copper complex that are detrimental to transparency and add undesirable color to the film.

Applicant's film is formed from a block copolymer made using an alkoxyamine. The core I of Applicant's claims comes from the scission of the alkoxyamines. Alkoxyamines are not

taught or suggested by the JP '167 reference and therefore the core I required in Applicant's block copolymer core from the alkoxyamine scission is not taught or suggested by the JP '167 reference.

The JP '167 reference further teaches away from Applicant's claims by teaching a difference process for obtaining the block copolymers.

The Examiner rejects claim 2, saying he has chosen an inorganic radical, so the organic radical goes away. Applicant notes that core I is an organic group, and Z is merely a polyfunctional radical attached to the organic group. Choosing Z as an inorganic group does not make organic core group I any less organic. Similarly the Akio reference to a zinc compound does not render claim 3 obvious, as the radical in claim 3 is still attached to an organic molecule.

For claim 4, as the Examiner notes the product by process claims only limit the structure – but that structure includes the core I of claim 1 which comes from the scission of the alkoxyamine – which is not taught or suggested by the JP '167 reference.

Claim 16 stands rejected under 35 U.S.C. §103(a) as being unpatentable over Akio et al (JP 2002194167 machine translation) in view of Kim (US 6,689,441).

As stated above, the Akio reference fails to teach or suggest Applicant's claims. The Kim reference is a secondary reference, cited for its teaching of a multilayer film. As with the Akio reference, the Kim reference also fails to teach or suggest a thermoformed film having a core (I) as claimed by Applicant. Thus the Kim reference fails to cure the defects of the Akio reference to teach or suggest all of Applicant's claim limitations.

Since the cited references fail to present a *prima facie* case of obviousness over the claims as amended, Applicant believes that the reasons for rejection have been overcome, and the claims herein should be allowable to the Applicant. Accordingly, reconsideration and allowance are requested.

Respectfully submitted,

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(54) FILM OR SHEET MOLDED FROM THERMOPLASTIC RESIN COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a film or a sheet obtained by molding a thermoplastic resin composition which has an excellent weatherability, moldability and flexibility, does not whiten when extended or bent and is capable of imparting transparency, when needed.

SOLUTION: The film or the sheet obtained by molding a thermoplastic resin composition consisting of (A) 5-95 wt.% of a copolymer comprising an acrylic acid ester and a methacrylic acid ester and (B) 95-5 wt.% of a block copolymer containing a methacrylic polymer block and an acrylic polymer block has an excellent flexibility and whitening resistance to bending or to extension and is capable of imparting transparency, when needed.

[Claims]

[Claim 1]

A film or sheet molded with a thermoplastic resin composition comprising (a) 5 to 95 % by weight of a copolymer of acrylic ester and methacrylic ester, and (b) 95 to 5 % by weight of a block copolymer containing methacrylic type polymer block and acrylic type polymer block.

[Claim 2]

The film or sheet of claim 1, wherein said copolymer (a) comprises a free polymer (a-1) and a core-shell type graft polymer (a-2) containing an inner layer (core) and an outer layer (shell).

[Claim 3]

The film or sheet of claim 1, wherein said copolymer (a) is a core-shell type graft polymer (a-3) containing an inner layer (core) and an outer layer (shell).

[Claim 4]

The film or sheet of claim 2 or 3, wherein said core of core-shell type graft polymer has a weight average particle size of 500-1900Å.

[Claim 5]

The film or sheet of claim 1, 2, 3 or 4, wherein said methacrylic type polymer block in the block copolymer (b) is made mainly of methyl methacrylate, while said acrylic polymer block is made mainly of butyl acrylate.

[Claim 6]

The film or sheet of claim 1, 2, 3, 4 or 5, wherein said block copolymer (b) is prepared by Atom Transfer Radical Polymerization technique.

[Detailed Description of Invention]

[0001]

[Field of Invention]

This invention relates to a film or sheet of a thermoplastic resin composition possessing improved weather-resistance, moldability, pliability and flexibility without whitening caused by stretching and bending operation, as well as possessing transparency.

[0002]

[Description of the Prior Art]

Methacrylic acid-ester type resin is excellent in weather-resistance and transparency and hence is used in various fields such as sheet and film and as a laminate for a various materials such as plastic, wood and metal for protecting substrate from deterioration, for maintaining appearance.

Usually, in such films or sheet of methacrylic acid-ester type resin, a rubber component is mixed to improve the moldability and impact-resistance, or a graft layer and a free polymer portion are softened in a graft polymerization, or compositions of the graft layer and of the free polymer portion are divided into several layers to improve the impact-resistance (see JP-47-13371-B1, JP-50-9022-B1). JP-59-36645-B1 and JP-59-36646-B1 propose to lower Tg of an inner layer of a rubber polymer component to higher than 10°C to improve the impact-resistance and bend-whitening.

[0003]

These solutions, however, are not sufficient to solve the problems of poor impact-resistance, breakage of laminated substrate and bend-whitening. Increase of a quantity of rubber component to improve the impact-resistance result in another problem of deterioration of moldability, transparency and permeation of plasticizer.

[0004]

[Problems to be solved by Invention]

An object of this invention is to provide a film or sheet of thermoplastic having excellent weather-resistance, moldability, pliability as well as transparency and has no whitening caused by tension and bending.

[0005]

[Means for solving the problem]

Inventors found a film or sheet that can solve the above-technical problems by combining a copolymer of an acrylic ester and methacrylic acid ester, and a block copolymer containing a methacrylic type polymer block and an acrylic polymer block.

(claims are repeated and hence are not translated)

[0006]

[Embodiment of Invention]

The copolymer (a) may be random copolymer, alternating copolymer, comb type graft copolymer having branch and trunk, core-shell type graft copolymer having inner layer (core) and outer layer (shell), copolymer obtained by additional polymerization of methacrylic acid ester containing acrylic ester in multistage polymerization in the presence of inner layer (core) consisting of acrylic ester and methacrylic acid ester, gradient copolymer produced by additional polymerization of a monomer mixture consisting of

acrylic ester and methacrylic acid ester, with changing compositions of acrylic ester and of methacrylic acid ester in multistage, and three-layer core-shell graft copolymer containing a central core, an interlayer and an outer layer, or they can be used in combination.

Preferable copolymer (a) comprises a free polymer (a-1) comprising random copolymer, alternating copolymer, graft copolymer and gradient copolymer, with a core-shell type graft copolymer (a-2) containing an inner layer (core) and an outer layer (shell) for obtaining film or sheet having improved moldability, transparency and anti-whitening under tension and bending, and with a core-shell type graft copolymer (a-3) containing an inner layer (core) and an outer layer (shell) for obtaining improved impact-resistance. These core-shell type graft copolymer (a-2) and (a-3) have preferably a weight average particle size of core of 500-1900Å for transparency.

[0007]

The free polymer (a-1) of this invention is a polymer having no gel part and may consist of random copolymer, alternating copolymer, graft copolymer or gradient copolymer. Random copolymer is preferred because of easy of polymerization.

Proportions of acrylic ester and methacrylic acid ester used for (a-1) are not limited specially but a ratio by weight of acrylic ester to methacrylic acid ester used is 5/95 to 95/5 of acrylic ester / methacrylic acid ester, from view points of glass transition temperature, refractive index, moldability, transparency, impact-resistance of (a-1) and to realize a balance of compatibility with the core-shell type graft polymer (a-2) or (a-3).

[0008]

The acrylic ester used for said free polymer (a-1) may be methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropylacrylate, n-butylacrylate, isobutyl acrylate, t-butylacrylate, n-pentylacrylate, n-hexylacrylate, cyclohexylacrylate, n-heptylacrylate, n-octylacrylate, 2-ethylhexylacrylate, nonylacrylate, decyl acrylate, dodecylacrylate, phenylacrylate, tolylacrylate, benzylacrylate, isobornylacrylate, 2-methoxy ethylacrylate, 3-methoxy butylacrylate, 2-hydroxyethylacrylate, 2-hydroxypropylacrylate, stearylacrylate, metaglycidyl acrylate, 2-aminoethylacrylate, gamma-(methacryloyl oxypropyl) trimethoxysilane, gamma-(methacryloyl oxypropyl) dimethoxymethylsilane, ethyleneoxide addition products of acrylic acid, trifluoromethyl methylacrylate, 2-trifluoro methylethylacrylate, 2-perfluoro ethylethylacrylate, 2-perfluoro ethyl-2-perfluoro butylethylacrylate, 2-perfluoro ethylacrylate, perfluoro methylacrylate, fluoromethylmethylacrylate, 2-perfluoro methyl-2-perfluoro ethylmethylacrylate, 2-perfluoro hexylethylacrylate, 2-perfluoro decylethylacrylate and 2-perfluoro hexadecylethylacrylate. From a view point of impact-resistance of film or sheet, acrylic acid alkyl ester and methglycidyl acrylate ester are preferred. From a view point of oil-resistance, 2-methoxy ethylacrylate, 3-methoxy butylacrylate, 2-hydroxyethylacrylate and 2-hydroxypropylacrylate are preferred. From a view point of polymerization speed, the carbon number of the alkyl group of acrylic acid alkyl ester is preferably 1-8 and may be methyl acrylate, ethyl acrylate, acrylic acid propyl, butyl acrylate, 2-ethylhexylacrylate, n-octylacrylate. They may be used alone or together two or more. Alkyl group of the acrylic acid alkyl ester can be linear or branched.

[0009]

Among them, n-butylacrylate is preferable for improving the impact-resistance and availability of the film or sheet. The methacrylic acid ester used for the free polymer (a-1) of this invention may be methyl methacrylate, ethyl methacrylate, n-propylmethacrylate, isopropyl methacrylate, n-butylmethacrylate, isobutylmethacrylate, t-butyl n-butylmethacrylate, n-pentylmethacrylate, n-hexylmethacrylate, cyclohexylmethacrylate, n-heptylmethacrylate, n-octylmethacrylate, 2-ethylhexylmethacrylate, nonyl methacrylate, decylmethacrylate, dodecylmethacrylate, phenylmethacrylate, toluylmethacrylate, benzylmethacrylate, isobornylmethacrylate, 2-methoxy ethylmethacrylate, 3-methoxy butylmethacrylate, 2-hydroxyethylmethacrylate, 2-hydroxypropylmethacrylate, stearyl methacrylate, glycidylmethacrylate, 2-aminoethylmethacrylate, gamma-(methacryloyl oxypropyl) trimethoxysilane, gamma-(methacryloyl oxypropyl)dimethoxymethylsilane, ethyleneoxide addition products of methacrylic acid, trifluoromethylmethacrylate, 2-trifluoromethylethylmethacrylate, 2-perfluoroethylethylmethacrylate, 2-perfluoroethyl-2-perfluorobutylethylmethacrylate, 2-perfluoroethylmethacrylate, perfluoromethyl methacrylate, fluoromethylmethacrylate, 2-perfluoro methyl-2-perfluoro ethylmethacrylate, 2-perfluoro hexylethylmethacrylate, 2-perfluoro decylethylmethacrylate and 2-perfluoro hexadecylethylmethacrylate. Glycidyl methacrylate and methacrylic acid alkyl ester are preferred to improve impact-resistance of the film or sheet, 2-methoxyethylmethacrylate, 3-methoxybutylmethacrylate, 2-hydroxyethylmethacrylate and 2-hydroxypropylmethacrylate are preferred to improve the oil resistance. To increase polymerization speed, a carbon number of alkyl group in the methacrylic acid alkyl ester is preferably 1-4 and the typical ones are for example methyl methacrylate, ethylmethacrylate, propylmethacrylate and butylmethacrylate. They may be used alone or in combination.

[0010]

The alkyl group of methacrylic acid alkyl ester may be linear or branched chain. Among the above-mentioned group, methylmethacrylate is preferred from the view point of moldability and availability.

[0011]

Examples of the combination of acrylic ester and methacrylic acid ester used for (a-1) are butyl acrylate/methyl methacrylate, ethyl acrylate/methyl methacrylate, ethyl acrylate / butylacrylate / 2-methoxy ethylacrylate / methyl methacrylate, butyl acrylate / stearylacrylate / methylmethacrylate, butyl acrylate/methylmethacrylate / glycidylmethacrylate, ethylacrylate / methylmethacrylate / glycidylmethacrylate, and ethylacrylate / butylacrylate / 2-methoxyethylacrylate / methylmethacrylate / glycidylmethacrylate/ Butylacrylate/methylmethacrylate is preferred from a view point of moldability and availability.

[0012]

Glass transition temperature (T_g) of the free polymer (a-1) of this invention is preferably 25-100°C from the viewpoints of moldability and pliability of film or sheet, and is more preferably 45-90 °C. Moldability will become poor if the glass transition temperature becomes lower than 25°C. On the other side, pliability or impact-resistance of film or sheet will be spoiled if it becomes higher than 100°C.

[0013]

The glass transition temperature (T_g) of polymer can be set by selecting proportions of monomers of polymer portion by using following Fox equation.

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} + \dots + \frac{W_m}{T_{gm}}$$

$$W_1 + W_2 + \dots + W_m = 1$$

in which T_g is the glass transition temperature of polymer portion, T_{g1} , T_{g2} , ..., T_{gm} are the glass transition temperatures of monomers, and W_1 , W_2 , ..., W_m are weight ratio of each monomer.

The glass transition temperature (T_g) can be measured by DSC (differential scanning calorimeter) or $\tan \delta$ peak of dynamic viscoelasticity.

[0014]

When the copolymer (a) consists of the free polymer (a-1) and a core-shell type graft polymer (a-2) containing an inner layer (core) and an outer layer (shell), the proportions of acrylic ester and methacrylic acid ester used for (a-2) are not limited but can be determined from the view points of the glass transition temperature of core and shell obtained, the total refractive index, moldability and a balance of compatibility with the free polymer (a-1) or the block copolymer (b).

Acrylic ester used for the core-shell type graft polymer (a-2) may be methylacrylate, ethylacrylate, n-propylacrylate, isopropylacrylate, n-butylacrylate, isobutylacrylate, t-butylacrylate, n-pentylacrylate, n-hexylacrylate, cyclohexylacrylate, n-heptylacrylate, n-octylacrylate, 2-ethylhexylacrylate, nonylacrylate, decylacrylate, dodecylacrylate, phenylacrylate, toluylacrylate, benzylacrylate, isobornylacrylate, 2-methoxyethylacrylate, 3-methoxybutylacrylate, 2-hydroxyethylacrylate, 2-hydroxypropylacrylate, stearylacrylate, metaglycidylacrylate, 2-aminoethylacrylate, gamma-(methacryloyloxypropyl)trimethoxysilane, gamma-(methacryloyloxypropyl)dimethoxymethylsilane, ethyleneoxide addition products of acrylic acid, trifluoromethylmethylacrylate, 2-trifluoromethylethylacrylate, 2-perfluoroethylethylacrylate, 2-perfluoro ethyl-2-perfluoro butylethylacrylate, 2-perfluoroethylacrylate, perfluoromethylacrylate, fluoromethylmethylacrylate, 2-perfluoromethyl-2-perfluoroethylmethylacrylate, 2-perfluoro hexylethylacrylate, 2-perfluoro decylethylacrylate and 2-perfluorohexadecylethylacrylate. From a view point of improvement in the impact-resistance of film or sheet obtained, acrylic acid alkyl ester and metaglycidyl acrylate ester are preferred. To increase the oil resistance, 2-methoxyethylacrylate, 3-methoxybutylacrylate, 2-hydroxyethylacrylate and 2-hydroxypropylacrylate are preferred. To improve polymerization speed, the carbon number of the alkyl group of acrylic acid alkyl ester is preferably 1-8 such as methylacrylate, ethylacrylate, propylacrylate, butylacrylate, 2-ethylhexylacrylate, n-octylacrylate. They can be used alone or in combination. Alkyl group of the acrylic acid alkyl ester can be linear or branched chain.

[0015]

Among them, n-butylacrylate is preferred from the viewpoint of impact-resistance and availability of film or sheet.

[0016]

The methacrylic acid ester used for the core-shell type graft polymer (a-2) may be

methylmethacrylate, ethylmethacrylate, n-propylmethacrylate, isopropylmethacrylate, n-butylmethacrylate, isobutylmethacrylate, t-butylmethacrylate, n-pentylmethacrylate, n-hexylmethacrylate, cyclohexylmethacrylate, n-heptylmethacrylate, n-octylmethacrylate, 2-ethylhexylmethacrylate, nonylmethacrylate, decylmethacrylate, dodecylmethacrylate, phenylmethacrylate, toluylmethacrylate, benzylmethacrylate, isobornylmethacrylate, 2-methoxyethylmethacrylate, 3-methoxybutylmethacrylate, 2-hydroxyethylmethacrylate, 2-hydroxypropylmethacrylate, stearylmethacrylate, glycidylmethacrylate, 2-aminoethylmethacrylate, gamma-(methacryloyloxypropyl)trimethoxysilane, gamma-(methacryloyloxypropyl)dimethoxymethylsilane, ethyleneoxide addition products of methacrylic acid, trifluoromethylmethacrylate, 2-trifluoromethylethyl methacrylate, 2-perfluoro ethylethylmethacrylate, 2-perfluoro ethyl-2-perfluoro butylethylmethacrylate, 2-perfluoro ethylmethacrylate, perfluoro methylmethacrylate, fluoromethylmethacrylate, 2-perfluoro methyl-2-perfluoro ethylmethacrylate, 2-perfluoro hexylethylmethacrylate, 2-perfluoro decylethylmethacrylate and 2-perfluoro hexadecylethylmethacrylate. From a view point of impact-resistance of film or sheet, glycidylmethacrylate and methacrylate are preferred. To increase oil-resistance, 2-methoxy ethylmethacrylate, 3-methoxy butylmethacrylate, 2-hydroxyethylmethacrylate and 2-hydroxypropylmethacrylate are preferred. To increase polymerization speed, a carbon number of the alkyl group of methacrylic acid alkyl ester is preferably 1-4, such as methyl methacrylate, ethylmethacrylate, propylmethacrylate and butyl methacrylate. They can be used alone or in combination.

[0017]

Examples of the combination of acrylic ester and methacrylic acid ester used for (a-2) may be butyl acrylate/methyl methacrylate, ethyl acrylate/methyl methacrylate, ethyl acrylate / butyl acrylate / 2-methoxy ethylacrylate / methyl methacrylate, butyl acrylate / stearylacrylate / methyl methacrylate, butyl acrylate/methyl methacrylate / glycidyl methacrylate, ethyl acrylate / methyl methacrylate / glycidyl methacrylate, and ethyl acrylate / butyl acrylate / 2-methoxy ethylacrylate / methyl methacrylate / glycidyl methacrylate. From the viewpoints of moldability and availability, butyl acrylate/methyl methacrylate is preferred.

[0018]

The alkyl group of the methacrylic acid alkyl ester may be linear or branched chain. To improve moldability and availability, methylmethacrylate is preferred.

[0019]

The acrylic ester and methacrylic esters used for the free polymer (a-1) and the core-shell type graft copolymer (a-2) may be different or same.

[0020]

The (a-1) and (a-2) can be mixed after each polymerization, or (a-2) is polymerized firstly and (a-1) is polymerized in the same polymerization tank. From the viewpoint of process and cost, it is preferred to polymerize firstly (a-1) and then (a-2) is polymerized in the same polymerization tank.

[0021]

From the view points of moldability and pliability of film or sheet obtained, the

core-shell type graft copolymer (a-2) of this invention have an outer layer (shell) whose glass transition temperature is preferably -35°C to 25°C and an inner layer (core) whose glass transition temperature is less than 25°C .

[0022]

The glass transition temperature (T_g) of the polymer can be adjusted by selecting proportions of monomers of polymer portion by using above-mentioned Fox equation. The glass transition temperature (T_g) can be measured by DSC (differential scanning calorimeter) or $\tan \delta$ peak of dynamic viscoelasticity.

[0023]

Proportions of core and shell in the core-shell type graft copolymer (a-2) are not limited specially but are preferably 10 to 80 % by weight of the core and 90 to 20 % by weight of the shell for the total of the graft copolymer (a-2), and more preferred the core is 20 to 65 % by weight and the shell is 80 to 35 % by weight. The impact-resistance will become poor if the core is less than 10 % by weight, while, if it exceeds 80 % by weight, there is such a tendency that mixing of the free polymer (a-1) with the block copolymer (b) becomes insufficient or non uniform.

[0024]

Proportions of the free polymer (a-1) and the core-shell type graft polymer (a-2) in the copolymer (a) are not limited specially but (a-1) is preferably 20 to 70 % by weight and (a-2) is preferably 80 to 30 % by weight for the total weight of copolymer (a), and more preferably (a-1) is 30 to 60 % by weight and (a-2) is 70 to 40 % by weight. If (a-1) exceeds 70 % by weight, resistance to whitening and pliability of film will be lowered, while if it is less than 20 % by weight, there is a tendency of lowering moldability.

[0025]

When said copolymer (a) is a core-shell type graft polymer (a-3) having an inner layer (core) and an outer layer (shell), proportions of the acrylic ester and methacrylic acid ester used for (a-3) are not limited specially but are determined from the view points the glass transition temperature of core and shell obtained (a-3), the total refractive index, moldability, and a balance of compatibility with free polymer (a-1) or block copolymer (b).

[0026]

The acrylic ester used for the core-shell type graft polymer (a-3) may be methylacrylate, ethylacrylate, n-propylacrylate, isopropylacrylate, n-butylacrylate, isobutylacrylate, t-butylacrylate, n-pentylacrylate, n-hexylacrylate, cyclohexylacrylate, n-heptylacrylate, n-octylacrylate, 2-ethylhexylacrylate, nonylacrylate, decylacrylate, dodecylacrylate, phenylacrylate, toluylacrylate, benzylacrylate, isobornylacrylate, 2-methoxyethylacrylate, 3-methoxybutylacrylate, 2-hydroxyethylacrylate, 2-hydroxypropylacrylate, stearylacrylate, metaglycidylacrylate, 2-aminoethylacrylate, gamma-(methacryloyloxypropyl)trimethoxysilane, gamma-(methacryloyloxypropyl)dimethoxymethylsilane, ethyleneoxide addition products of acrylic acid, trifluoromethylmethylacrylate, 2-trifluoromethylethylacrylate, 2-perfluoroethylethylacrylate, 2-perfluoroethyl-2-perfluorobutylethylacrylate, 2-perfluoroethylacrylate, perfluoromethylacrylate, fluoromethylmethylacrylate, 2-perfluoromethyl-2-perfluoroethylmethylacrylate, 2-perfluorohexylethylacrylate, 2-perfluorodecylethylacrylate and 2-perfluorohexadecyl

ethylacrylate. To improve the impact resistance of film or sheet, acrylic acid alkyl ester and metaglycidylacrylate are preferred. To increase the oil resistance, 2-methoxyethylacrylate, 3-methoxybutylacrylate, 2-hydroxyethylacrylate and 2-hydroxypropylacrylate are preferred. To increase the polymerization speed, a carbon number of the alkyl group of the acrylate is preferably 1-8 such as methylacrylate, ethylacrylate, propylacrylate, butylacrylate, 2-ethylhexylacrylate and n-octylacrylate. They can be used alone or in combination. The alkyl group of the acrylic acid alkyl ester may be linear or branched chain.

[0027]

From a view point of impact resistance of film or sheet and availability, n-butylacrylate is preferred.

[0028]

The methacrylic acid ester used for the core-shell type graft polymer (a-3) of this invention may be methylmethacrylate, ethylmethacrylate, n-propylmethacrylate, isopropylmethacrylate, n-butylmethacrylate, isobutylmethacrylate, t-butylmethacrylate, n-pentylmethacrylate, n-hexylmethacrylate, cyclohexylmethacrylate, n-heptylmethacrylate, n-octylmethacrylate, 2-ethylhexylmethacrylate, nonylmethacrylate, decylmethacrylate, dodecylmethacrylate, phenylmethacrylate, toluylmethacrylate, benzylmethacrylate, isobornylmethacrylate, 2-methoxyethylmethacrylate, 3-methoxybutylmethacrylate, 2-hydroxyethylmethacrylate, 2-hydroxypropylmethacrylate, stearylmethacrylate, glycidylmethacrylate, 2-aminoethylmethacrylate, gamma-(methacryloyloxypropyl) trimethoxysilane, gamma-(methacryloyloxypropyl)dimethoxymethylsilane, ethyleneoxide addition products of methacrylic acid, trifluoromethylmethylmethacrylate, 2-trifluoromethylethylmethacrylate, 2-perfluoroethylethylmethacrylate, 2-perfluoroethyl-2-perfluorobutylethylmethacrylate, 2-perfluoroethylmethacrylate, perfluoromethylmethacrylate, fluoromethylmethylmethacrylate, 2-perfluoromethyl-2-perfluoroethylmethylmethacrylate, 2-perfluorohexylethylmethacrylate, 2-perfluorodecylethylmethacrylate and 2-perfluorohexadecylethylmethacrylate. To improve the impact resistance of film or sheet, glycidylmethacrylate and methacrylic acid alkyl ester are preferred. To increase the oil resistance, 2-methoxyethylmethacrylate, 3-methoxybutylmethacrylate, 2-hydroxyethylmethacrylate and 2-hydroxypropylmethacrylate are preferred. To improve the polymerization speed, a carbon number of the alkyl group of methacrylic acid alkyl ester is preferably 1-4 such as methylmethacrylate, ethylmethacrylate, propylmethacrylate and butylmethacrylate. They can be used alone or in combination. The alkyl group of methacrylic acid alkyl ester can be linear or branched chain. Among them, methylmethacrylate is preferred from the view point of moldability of film and availability.

[0029]

Examples of combination the acrylic ester and methacrylic acid ester used for (a-3) are butylacrylate/methylmethacrylate, ethylacrylate/methylmethacrylate, ethylacrylate/butylacrylate / 2-methoxyethylacrylate/methylmethacrylate, butylacrylate/stearylacrylate/methylmethacrylate, butylacrylate/methylmethacrylate/glycidylmethacrylate, ethylacrylate/methylmethacrylate/glycidylmethacrylate, and ethylacrylate/butylacrylate/2-methoxyethylacrylate/

methylmethacrylate/glycidylmethacrylate. Among them, from the view point of moldability of film and availability, butylacrylate/methylmethacrylate is preferred.

[0030]

From the view point of pliability of film or sheet and impact resistance, the core-shell type graft copolymer (a-3) of this invention have the glass transition temperature of lower than 25°C for the inner layer (core) and the glass transition temperature of higher than 25°C for the outer layer (shell).

[0031]

The glass transition temperature (T_g) of the polymer can be adjusted by selecting the proportions by weight of monomers of polymer portion according to the aforementioned Fox equation. The glass transition temperature (T_g) is measured by DSC (differential scanning calorimeter) or the tan delta peak of dynamic viscoelasticity.

[0032]

Proportions of the core and a shell in the core-shell type graft copolymer (a-3) are not limited specially but the core is preferably 10 to 80 % by weight and the shell is 90 to 20 % by weight on the basis by weight of the total graft copolymer (a-3), and more preferably the core is 20 to 65 % by weight and the shell is 80 to 35 % by weight. If the proportion of the core is not higher than 10 % by weight, the impact-proof will become poor while if it exceeds 80 % by weight, dispersion during mixing with the block copolymer (b) will becomes insufficient.

[0033]

The core-shell type graft copolymer (a-3) can be combining with the free polymer (a-1), when its dispersion is insufficient at the mixing with the block copolymer (b) or if moldability is not good.

[0034]

A weight average particle size of the core of the core-shell type graft polymer (a-2) and (a-3) is in a range of 300-3000 Å, preferably 400-2500Å, more preferably 500-1900Å. If the weight average particle size is not higher than 300 Å, the impact resistance will be lowered. On the contrary, if the weight average particle size exceeds 3000 Å, the moldability of film or sheet becomes poor or transparency of film or sheet will be lowered. The weight average particle size is measured by dynamic light scattering.

[0035]

The core of the core-shell type graft copolymer (a-2) and (a-3) may contain cross-linking agent mentioned later and/or a portion originating from a graft crossing agent.

[0036]

The cross-linking agent is a compound, which has two or more functional groups in a molecular, the reactivity of the functional groups being equal. The graft-crossing agent is a compound, which has two or more functional groups in a molecular, the reactivity of the functional groups being different. The cross-linking agent is used to form cross-linked bond in the same polymer component, while the graft crossing agent is used to produce crossing between different polymer components. However, in actual uses, classification of the cross-linking agent and of the graft crossing agent is not so clear, so that the cross-linking agent forms the cross linkage between different polymer components

and the graft crossing agent may forms the cross linking bond in the same polymer component.

[0037]

Examples of the cross-linking agent and/or the graft crossing agent may be ethyleneglycoldimethacrylate, dimethyleneglycoldimethacrylate, dipropyleneglycol dimethacrylate or those in which methacrylate is changed to acrylate, vinyl-group containing polyfunctional monomers such as divinylbenzene and divinyladipate, allyl-group containing polyfunctional monomers such diallyl phthalate, diallyl maleate, allyl acrylate, allyl methacrylate, triaryl cyanurate and triallyl isocyanurate. They can be used alone or in combinationm.

[0038]

A gel content of (a-2) and (a-3) and the graft rate of the resin monomers are influenced by the cross linking agent and/or the graft crossing agent affect. An amount of the polyfunctional monomer is 0.1 to 20 parts by weight, preferably 0.5 - 10 parts by weight to 100 part by weight of monomers used for (a-2) and (a-3). If the content is less than 0.1 parts by weight, transparency or resistance to permeation of plasticizer become poor and if it exceeds 20 parts by weight, ductility and impact-resistance will be spoiled.

[0039]

When transparency of film or sheet is required, the transparency can be realized by adjusting the refractive index of a copolymer (a) to the refractive index of the block copolymer (b) used. A difference of the refractive index between copolymer (a) and the block copolymer (b) is preferably less than 0.1, more preferred less than 0.05. If higher transparency of film or sheet is required, the difference is preferably less than 0.01. The refractive index (nD) of the copolymer (a) can be adjusted by selecting weight ratios of monomers of the polymer according to the following formula:

$$(nD) = (nD_1 + nD_2 + \dots + nD_m) / (W_1 + W_2 + \dots + W_m)$$

$$W_1 + W_2 + \dots + W_m = 1$$

(in which, nD is the refractive index of the polymer, nD₁, nD₂, --, nD_m are respective refractive index of each monomer and W₁, W₂, --, W_m are the weight ratio of the monomers, The refractive index (nD) of the polymer is measured by a light source using D line of a sodium lamp)

The copolymer (a) of this invention can be prepared by any known technique such as suspension polymerization and emulsion polymerization and the emulsion polymerization is preferred from a view point of the cost and easy to remove reaction heat.

[0040]

In the emulsion polymerization, a usual polymerization initiator, which generates free radicals, is used. Example of the polymerization initiator may be inorganic peroxides such as sodium persulfate and potassium persulfate and organic peroxide such as cumene hydroperoxide and benzoyl peroxide. Oil-soluble initiators such as azobisisobutyronitrile also can be used. They can be used alone or in combination.

[0041]

These polymerization initiators may be used as Redox type polymerization initiator in which they are combined with a reducing agent such as sodium sulfite, sodium

subulfite, sodium formaldehyde sulfoxylate, ascorbic acid and ferrous sulfate.

[0042]

Any surface-active agent can be in the emulsion polymerization. The surface-active agent can be usual ones for emulsion polymerization such as anionic detergents such as sodium alkyl-sulfate, sodium alkylbenzene-sulfate and sodium laurate and nonion surfactants such as a reaction product of alkylphenol and ethyleneoxide. These surface-active agents can be used alone or in combination. If necessary, cationic surfactants such as alkylamine hydrochloride may be used.

[0043]

The resin composition is separated and recovered from a he polymer latex obtained by usual solidification technique (for example, with salt) and washing, or by spraying, freeze-drying or the like.

[0044]

The block copolymer (b) containing the meta-acrylic polymer block and the acrylic polymer block used in this invention is a block copolymer containing at least one polymer block (A) consisting mainly of methacrylic monomer and at least one polymer block (B) consisting mainly of acrylic monomer respectively.

[0045]

The block copolymer (b) is at least one block copolymers chosen from A-B type di-block copolymer, A-B-A type tri-block copolymer, B-A-B type tri-block copolymer and (A-B)_n type multi-block copolymer. Among them, the A-B type di-block copolymer and A-B-A type tri-block copolymer or their mixtures are preferred from a viewpoint of moldability or pliability of film or sheet.

[0046]

The block copolymer (b) has a structure of linear block copolymer or branched (star) block copolymer or their mixture. The structure of block copolymer can be selected according to characteristics required, such as processability of thermoplastic resin composition and mechanical properties.

[0047]

A number average molecular weight of the block copolymer (b) is not limited specially but is 30000-500000 and more preferably 50000-400000. Since there is a tendency for viscosity to become high when viscosity is low when a number average molecular weight is small, and a number average molecular weight is large, it is set up according to the working characteristic to need. A molecular weight makes chloroform a mobile phase and is measured by polystyrene conversion by the GPC method using a polystyrene gel column.

[0048]

A ratio (M_w/M_n) of a weight average molecular weight (M_w) to a number average molecular weight (M_n) is measured by the gel permeation chromatography of the block copolymer (b) and is not limited specially but is preferably lower than 1.8 and more preferably lower than 1.5. If the M_w/M_n exceeds 1.8, homogeneity of the block copolymer will be lost.

[0049]

Proportions of the methacrylic polymer block (A) to the acrylic polymer block (B) in the block copolymer (b) are 5 to 95 % by weight of the block (A) and 95 to 5 % by weight of the block (B). To improve moldability, pliability, whitening-resistance of film or sheet, (A) is preferably 10 to 80 % by weight and (B) is 90 to 20 % by weight, more preferably, (A) is 20 to 70 % by weight and (B) is 80 to 30 % by weight. If the proportions of (A) decreases lower than 5 % by weight, the moldability of film or sheet will become poor. If the proportion of (B) decrease low than 10 % by weight, the pliability of film or sheet will be lost so that resistance to whitening become poor when they are tensioned and bend.

[0050]

The meta-acrylic polymer block (A) which constitutes a block copolymer (b) consists of 50 to 100 % by weight of methacrylic acid ester, and this and 0 to 50 % by weight of copolymerizable vinyl type monomers.

[0051]

The methacrylic acid ester in (A) may be methylmethacrylate, ethylmethacrylate, n-propylmethacrylate, isopropylmethacrylate, n-butylmethacrylate, isobutylmethacrylate, tert-butylmethacrylate, n-pentylmethacrylate, n-hexylmethacrylate, cyclohexylmethacrylate, n-heptylmethacrylate, n-octylmethacrylate, 2-ethylhexylmethacrylate, nonylmethacrylate, decylmethacrylate, dodecylmethacrylate, phenylmethacrylate, toluylmethacrylate, benzylmethacrylate, isobornylmethacrylate, 2-methoxyethylmethacrylate, 3-methoxybutylmethacrylate, 2-hydroxyethylmethacrylate, 2-hydroxypropylmethacrylate, stearylmethacrylate, glycidylmethacrylate, 2-aminoethylmethacrylate, gamma-(methacryloyl oxypropyl)trimethoxysilane, gamma-(methacryloyl oxypropyl)dimethoxymethylsilane, ethyleneoxide addition products of methacrylic acid, trifluoromethylmethylmethacrylate, 2-trifluoromethylethylmethacrylate, 2-perfluoroethylmethacrylate, 2-perfluoroethyl-2-perfluorobutylethylmethacrylate, 2-perfluoroethylmethacrylate, perfluoromethylmethacrylate, fluoromethylmethylmethacrylate, 2-perfluoromethyl-2-perfluoroethylmethylmethacrylate, 2-perfluorohexylethylmethacrylate, and 2-perfluorodecylethylmethacrylate, 2-perfluorohexadecylethylmethacrylate. They can be used alone or in combination. Among them, methylmethacrylate is preferred from a view point of availability.

[0052]

The vinyl monomer copolymerizable with the methacrylic acid ester in (A) may be various vinyl monomers such as acrylic esters such as methylacrylate, ethylacrylate, n-propylacrylate, isopropylacrylate, n-butylacrylate, isobutyl acrylate, t-butylacrylate, n-pentylacrylate, n-hexylacrylate, cyclohexylacrylate, n-heptylacrylate, n-octylacrylate, 2-ethylhexylacrylate, nonylacrylate, decyl acrylate, dodecylacrylate, phenylacrylate, toluylacrylate, benzylacrylate, isobornylacrylate, 2-methoxyethylacrylate, 3-methoxybutylacrylate, 2-hydroxyethylacrylate, 2-hydroxypropylacrylate, stearylacrylate, glycidylacrylate, 2-aminoethylacrylate, gamma-(methacryloyloxypropyl)trimethoxysilane, gamma-(methacryloyloxypropyl) dimethoxymethylsilane, ethyleneoxide addition products of acrylic acid, trifluoromethylmethylacrylate, 2-trifluoromethylethylacrylate, 2-perfluoroethyl ethylacrylate, 2-perfluoroethyl-2-perfluorobutylethylacrylate,

2-perfluoroethylacrylate, perfluoromethylacrylate, fluoromethylmethylacrylate, 2-perfluoromethyl-2-perfluoro ethylmethylacrylate, 2-perfluorohexylethylacrylate, 2-perfluorodecylethylacrylate and 2-perfluoro hexadecylethylacrylate; aromatic alkenyl compounds such as styrene, alpha-methylstyrene, p-methylstyrene and p-methoxy styrene; vinyl cyanide compounds such as acrylonitrile and methacrylonitrile; conjugated diene compounds such as butadiene and isoprene; halogenated unsaturated compounds such as vinylidene fluoride, vinylidene chloride, perfluoroethylene, perfluoropropylene; silicon-containing unsaturated compounds such as vinyltrimetoxysilane and vinyltriethoxysilane; unsaturated dicarboxylic acid compounds such as maleic anhydrides, maleic acid and monoalkyl ester and dialkyl ester of maleic acid and, fumaric acid, monoalkyl ester of fumaric acid and dialkyl ester; vinyl ester compounds such as vinyl acetate, vinyl propionate, vinyl pivalate, vinyl benzoate and vinyl cinnamate; maleimide compounds such as maleimide, methylmaleimide, ethylmaleimide, propylmaleimide, butylmaleimide, hexylmaleimide, octylmaleimide, dodecylmaleimide, stearylmaleimide, phenylmaleimide and cyclohexylmaleimide. They can be used alone or in combination and can be selected from a view point of compatibility with the copolymer (a).

[0053]

The glass transition temperature of (A) is not lower than 25°C, preferably not lower than 40°C and more preferably not lower than 50°C. If the glass transition temperature becomes lower than 25°C, the moldability and heat-resistance of film or sheet will be lowered.

[0054]

The acrylic polymer block (B) in the block copolymer (b) comprises preferably 50 to 100 % by weight of acrylic ester and 0 to 50 % by weight of copolymerizable vinyl monomers.

[0055]

The acrylic ester in (B) may be methylacrylate, ethylacrylate, n-propylacrylate, isopropylacrylate, n-butylacrylate, isobutylacrylate, t-butylacrylate, n-pentylacrylate, n-hexylacrylate, cyclohexylacrylate, n-heptylacrylate, n-octylacrylate, 2-ethylhexylacrylate, nonylacrylate, decylacrylate, dodecylacrylate, phenylacrylate, toluylacrylate, benzylacrylate, isobornylacrylate, 2-methoxyethylacrylate, 3-methoxybutylacrylate, 2-hydroxyethylacrylate, 2-hydroxypropylacrylate, stearylacrylate, glycidylacrylate, 2-aminoethylacrylate, gamma-(methacryloyloxypropyl)trimethoxysilane, gamma-(methacryloyloxypropyl)dimethoxymethylsilane, ethyleneoxide addition products of acrylic acid, trifluoromethylmethylacrylate, 2-trifluoromethylethylacrylate, 2-perfluoroethylethyl acrylate, 2-perfluoroethyl-2-perfluorobutylethylacrylate, 2-perfluoroethylacrylate, perfluoromethylacrylate, fluoromethylmethylacrylate, 2-perfluoromethyl-2-perfluoro ethylmethylacrylate, 2-perfluoro hexylethylacrylate, 2-perfluorodecylethylacrylate and 2-perfluoro hexadecylethylacrylate. They can be used alone or in combination. Among them, n-butylacrylate is preferred from the view point of pliability and resistance to whitening of film or sheet and availability.

[0056]

The vinyl monomer copolymerizable with the acrylic ester in the block (B) may be

various vinyl monomers such as methacrylic acid esters such as methylmethacrylate, ethylmethacrylate, n-propylmethacrylate, isopropylmethacrylate, n-butylmethacrylate, isobutylmethacrylate, t-butylmethacrylate, n-pentylmethacrylate, n-hexylmethacrylate, cyclohexylmethacrylate, n-heptylmethacrylate, n-octylmethacrylate, 2-ethylhexylmethacrylate, nonylmethacrylate, decylmethacrylate, dodecylmethacrylate, phenylmethacrylate, toluylmethacrylate, benzylmethacrylate, isobornylmethacrylate, 2-methoxyethylmethacrylate, 3-methoxybutylmethacrylate, 2-hydroxyethylmethacrylate, 2-hydroxypropylmethacrylate, stearylmethacrylate, glycidylmethacrylate, 2-aminoethylmethacrylate, gamma-(methacryloyloxypropyl)trimethoxysilane, gamma-(methacryloyl oxypropyl)dimethoxymethylsilane, ethyleneoxide addition precuts of methacrylic acid, trifluoromethylmethacrylate, 2-trifluoromethylethylmethacrylate, 2-perfluoroethylethylmethacrylate, 2-perfluoroethyl-2-perfluorobutylethylmethacrylate, 2-perfluoroethylmethacrylate, perfluoromethylmethacrylate, fluoromethylmethylmethacrylate, 2-perfluoromethyl-2-perfluoroethylmethylmethacrylate, 2-perfluoro hexylethylmethacrylate, 2-perfluorodecylethylmethacrylate and 2-perfluoro hexadecylethylmethacrylate; aromatic alkenyl compounds such as styrene, alpha-methylstyrene, p-methylstyrene and p-methoxy styrene; vinyl cyanide compounds such as acrylonitrile and methacrylonitrile; conjugated diene compound such as butadiene and isoprene; halogen-containing unsaturated compounds such as vinyl chloride, vinylidene chloride, perfluoroethylene, perfluoropropylene and vinylidene fluoride; silicon containing unsaturated compounds such as vinyltrimetoxysilane and vinyltriethoxysilane; unsaturated dicarboxylic acid compounds such as maleic anhydride, maleic acid and monoalkyl ester and dialkyl ester of maleic acid, fumaric acid and monoalkyl ester and dialkyl ester of fumaric acid; vinyl ester compounds such as vinyl acetate, vinyl propionate, vinyl pivalate, vinylbenzoate and vinyl cinnamate; maleimide compounds such as maleimide, methylmaleimide, ethylmaleimide, propylmaleimide, butylmaleimide, hexylmaleimide, octylmaleimide, dodecylmaleimide, stearylmaleimide, phenylmaleimide and cyclohexylmaleimide. They can be used alone or in combination. These vinyl monomers can be selected so that the block (B) have a desired glass-transition temperature. The glass-transition temperature of (B) is lower than 25°C, preferably lower than 0°C, more preferably lower than -20°C. If the glass-transition temperature becomes higher than 25°C, the pliability of film or sheet and resistance to whitening will become poor.

[0057]

The block copolymer (b) can be prepared by any known method but it is preferred to use a controlled polymerization technique. The controlled polymerization technique may be living anionic polymerization, radical polymerization using chain transfer agent and living radical polymerization developed recently. The living radical polymerization is preferred from a viewpoint of molecular weight of the block copolymer and of control of structure.

[0058]

The living radical polymerization is a radical polymerization in which activity of polymerization terminal is not lost but is maintained. In the living polymerization, activity of terminal is continued always in a narrow sense, but the living polymerization of

this invention includes a pseudo-living polymerization in which terminals inactivated and terminals in active are in an equilibrium condition, as usually accepted. Many researchers study the living radical polymerization actively recently. Examples of the living radical polymerization include techniques using chain transfer agent such as polysulfide, cobalt porphyrin complex (J. Am.Chem.Soc.1994, 116, 7943), or using a radical scavenger such as nitroxide compound (Macromolecules, 1994, 27, 7228) and Atom Transfer Radical Polymerization (ATRP) in which organic halogenated compound is used as an initiator and a transition metal complex is used as catalyst. Any technique can be used in this invention but ATRP is preferred from a view point of ease of control.

[0059]

In the atom transfer radical polymerization technique, polymerization is effected in the presence of catalyst consisting of a metal complex having elements of Group 8, 9, 10 or 11 of the periodic table as main metal and an initiator of organo halogenated compound or sulfonyl halide compound (see, Matyjaszewski et al., J.Am.Chem.Soc.1995, 117 and 5614, Macromolecules 1995, 28, and 7901, Science 1996, 272, and 866, or Sawamoto et al. Macromolecules1995, 28, 1721). This technique permits to advances the polymerization in living mode even in the radical polymerization process in which termination reactions such as radical coupling occur easily, and to obtain a polymer having a narrow molecular weight distribution of about $M_w/M_n = 1.1 - 1.5$. The molecular weight can be controlled freely by selecting initial proportions of monomer and initiator.

[0060]

The organo halogenated compound or sulfonyl halide compound used as initiator in the atom transfer radical polymerization process may be monofunctional, bifunctional or polyfunctional compound and is used according to purpose. When diblock copolymer is desired, monofunctional compound is preferred. If A-B-A triblock copolymer or B-A-B type triblock copolymer is desired, bifunctional compound is preferred. When a branched block copolymer is desired, polyfunctional compound is used.

[0061]

The monofunctional compound may be compounds having a formula: $C_6H_5-CH_2X$, $C_6H_5-C(H)(X)-CH_3$, $C_6H_5-C(X)(CH_3)_2$, $R^1-C(H)(X)-COOR^2$ and $R^1-C(CH_3)(X)-COOR^2$, $R^1-C(H)(X)-CO-R^2$, $R^1-C(CH_3)(X)-CO-R^2$, $R^1-C_6H_4-SO_2X$ (in which C_6H_4 is phenylene group (o-, m or p-substitution), R^1 is H or alkyl group of a carbon number of 1-20, aryl group of a carbon number of 6-20, or aralkyl group of a carbon number of 7-20, X is chlorine, bromine or iodine, and R^2 is an organic group of monovalence of a carbon number of 1-20).

[0062]

The bifunctional compound may be compounds having a Formula: $X-CH_2-C_6H_4-CH_2-X$, $X-CH(CH_3)-C_6H_4-CH(CH_3)-X$, $X-C(CH_3)_2-C_6H_4-C(CH_3)_2-X$, $X-CH(COOR^3)-(CH_2)_n-CH(COOR^3)-X$, $X-C(CH_3)(COOR^3)-(CH_2)_n-C(CH_3)(COOR^3)-X$, $X-CH(COR^3)-(CH_2)_n-CH(COR^3)-X$, $X-C(CH_3)(COR^3)-(CH_2)_n-C(CH_3)(COR^3)-X$, $X-CH_2-CO-CH_2-X$, $X-CH(CH_3)-CO-CH(CH_3)-X$, $X-C(CH_3)_2-CO-C(CH_3)_2-X$, $X-CH(C_6H_5)-CO-CH(C_6H_5)-X$, $X-CH_2-COO-(CH_2)_n-OCO-CH_2-X$, $X-CH(CH_3)-COO-(CH_2)_n-OCO-CH(CH_3)-X$, $X-C(CH_3)_2-COO-(CH_2)_n-OCO-C(CH_3)_2-X$,

$X-CH_2-CO-CO-CH_2-X$, $X-CH(CH_3)-CO-CO-CH(CH_3)-X$, $X-C(CH_3)_2-CO-CO-C(CH_3)_2-X$, $X-CH_2-COO-C_6H_4-OCO-CH_2-X$, $X-CH(CH_3)-COO-C_6H_4-OCO-CH(CH_3)-X$, $X-C(CH_3)_2-COO-C_6H_4-OCO-C(CH_3)_2-X$, $X-SO_2-C_6H_4-SO_2-X$ (in which, R^3 is alkyl group of a carbon number of 1-20, aryl group of a carbon number of 6-20 or aralkyl group of a carbon number of 7-20, C_6H_4 is phenylene group (o, m- or p- substitution), C_6H_5 is phenyl group, n is an integer of 0-20, and X is chlorine, bromine or iodine).

[0063]

The polyfunctional compound may be compounds having a formula: $C_6H_3-(CH_2-X)_3$, $C_6H_3-(CH(CH_3)-X)_3$, $C_6H_3-(C(CH_3)_2-X)_3$, $C_6H_3-(OCO-CH_2-X)_3$, $C_6H_3-(OCO-CH(CH_3)-X)_3$, $C_6H_3-(OCO-C(CH_3)_2-X)_3$ and $C_6H_3-(SO_2-X)_3$ (in which C_6H_3 is a 3 substituted-phenyl group (1- or 6- substitution), and X is chlorine, bromine or iodine).

[0064]

Other organo halogenated compound or sulfonyl halide compound than the polymerization initiator can be used to obtain easily a polymer having a functional group at terminal. Such functional group may be alkenyl, hydroxyl, epoxy, amino, amide, silyl group or the like.

[0065]

In the organic halogenated compound or sulfonyl halide compound used as initiator, a carbon to which a halogen bonds is bond to a carbonyl group or a phenyl group, and a carbon-halogen bond is activated to start polymerization. An amount of the initiator be used is determined according to the molecular weight of block copolymer required. That is, the molecular weight of block copolymer can be controlled by selecting a number of monomers per one molecule of initiator.

[0066]

The transition metal complex used as catalyst used in the atom transfer radical polymerization is not limited specially but may be complex of monovalent and divalent copper, divalent ruthenium, divalent iron or divalent nickel. The copper complex is more preferred from the view point of cost or reaction controllability.

[0067]

The monovalent copper compound may be copper chloride, copper bromide, copper iodide, copper cyanide, copper oxide and copper perchloride. When a copper compound is used, 2,2'-bipyridyl and its derivative, 1,10-phenanthroline and its derivative and polyamine such as tetramethyl ethylenetriamine (TMEDA), pentamethyl diethylenetriamine and hexamethyl(2-aminoethyl) amine or the like may be added as a ligand to improve catalytic activity. Tris(phenyl) phosphine complex ($RuCl_2(PPh_3)_3$) of divalent ruthenium chloride also is preferred as catalyst. When a ruthenium compound is used as catalyst, aluminum alkoxides may be added as an activator. Divalent iron triphenyl phosphine complex ($FeCl_2(PPh_3)_2$), divalent nickel triphenyl phosphine complex ($NiCl_2(PPh_3)_2$) and divalent nickel tributyl phosphine complex ($NiBr_2(PBu_3)_2$) also are preferred as catalyst. Amounts of catalyst, ligand and activator to be used are not limited specially. Amounts of initiator, monomer and solvent to be used are determined can be determined from a reaction velocity required.

[0068]

The atom transfer radical polymerization can be performed without solvent (bulk polymerization) or in solvent. The solvent may be hydrocarbon solvent such as benzene and toluene; ether type solvents such as diethylether, tetrahydrofuran; halogenated hydrocarbon solvents such as methylene chloride and chloroform; ketone solvent such as acetone, methylethyl ketone and methyl isobutyl ketone; alcoholic solvent such as methanol, ethanol, propanol, isopropanol, n-butanol and t-butanol; nitrile type solvent such as acetonitrile, propionitrile and benzonitrile; ester solvent such as ethylacetate and butyl acetate; and carbonate solvents such as ethylene carbonate and propylene carbonate. They can be used alone or in combination. What solvent is used, an amount of solvent is determined from a view point of viscosity which permits effective agitation (or, reaction velocity).

[0069]

The polymerization can be performed in a range between ambient temperature to 200°C, preferably 50-150°C.

[0070]

To prepare a block copolymer by the polymerization technique, monomers are added successively, a polymer is prepared firstly and the polymer is used as high-polymer initiator, or polymers are prepared beforehand and then they are reacted later. These techniques can be selected freely from the view point of purpose. The successive addition method is preferred because of simplicity.

[0071]

Proportions of the copolymer (a) and of the block copolymer (b) are 5 to 95 % by weight for the copolymer (a) and 95 to 5 % by weight for the block copolymer (b). To improve moldability, pliability and resistance to whitening of film or sheet, (a) is preferably 30 to 70 % by weight and (b) is preferably 70 to 30 % by weight. If the proportion of the block copolymer (b) becomes lower than 5% weight, improvement in moldability, pliability and resistance to whitening of film or sheet become poor. If the proportion of the block copolymer (b) becomes higher than 95% weight, there is a tendency that the moldability become poor. There is no limitation in thickness of film or sheet but generally the film has a thickness of about 1-300 micrometers and the sheet has a thickness of about 300 micrometers to 20 mm.

[0072]

The thermoplastic resin composition consisting of copolymer (a) and block copolymer (b) of this invention can be produced by any known technique such as mechanical mixing such as Banbury mixer, roll mill and twin screw extruder. The resulting pellets can be used in a wide range of temperature.

[0073]

The thermoplastic resin composition may contain other polymers, stabilizer, plasticizer, lubricant, fire retardant, pigments, bulking agent, in addition to the copolymer (a) and the block copolymer (b) if needed. Examples are polymer such as polybutene rubber, polyisobutylene rubber, EPR and EPDM; stabilizer such as triphenyl phosphite, hindered phenol and dibutyltin maleate; plasticizers such as paraffin oil, polybutene oil, gas oil, spindle oil, machining oil, linseed oil, sesame oil, castor oil, camellia oil, dioctyl phthalate,

dibutyl phthalate, dioctyl adipate and tricresyl phosphate; lubricant such as polyethylene wax, polypropylene wax and montanic acid type wax and triphenyl phosphate; fire retardant such as tricresylphosphate, decabromobiphenyl, decabromobiphenyl ether and antimonous oxide; paints such as titanium oxide, zinc sulfide and a zinc oxide; fillers such as glass fibers, asbestos, wollastonite, mica, talc and calcium carbonate.

[0074]

The film or sheet of the thermoplastic resin composition can be produced by known method such as extrusion, compression, blow, calender molding, vacuum forming and injection molding. Extrusion molding method is preferred from a view point of processability and cost. Material is melt-extruded from a T die or a ring die at desired shape and size and is cooled. It is also possible to effect mono- or bi-axial stretching simultaneous with extrusion.

[0075]

Followings are illustration of physical properties required in the invention. However, the scope of invention is not limited to them.

[0076]

In a film or sheet possessing excellent balance in transparency, pliability and resistance to whitening according to this invention, the free polymer (a-1), the core-shell block copolymer (a-2) and the block copolymer (b) consist of n-butylacrylate and methylmethacrylate, (a-1) has a glass transition temperature of 60-80°C, proportions of core and a shell in (a-2) are 60 % by weight of core and 40 % by weight of shell on the base of total weight of (a-2), proportions of (a-1) and (a-2) in the copolymer (a) are 50 % by weight of (a-1) and 50 % by weight of (a-2) on the base of total weight of (a), proportions of the methacrylic polymer block (A) and an acrylic polymer block (B) in the block (b) are 30 % by weight of (A) and 70 % by weight of (B), and proportions of the copolymer (a) and the block copolymer (b) are 55% by weight of (a) and 45 % by weight of (b) on the base of total weight of the thermoplastic composition.

[0077]

When a film or sheet possessing improved impact-resistance and pliability is requested, it is preferred to use a material in which the core-shell type block copolymer (a-3) and the block copolymer (b) consist of n-butylacrylate and methylmethacrylate, and proportions of the core and shell in (a-3) are 50 % by weight of core and 50 % by weight of shell on the base of the total weight of (a-3), proportions of methacrylic polymer block (A) and acrylic polymer block (B) in block (b) are 30 % by weight of (A) and 70 % by weight of (B) on the base of the total weight of (b), and proportions of the copolymer (a) and the block body (b) are 55% by weight of (a) and 45 % by weight of (b) on the basis of the total weight of the thermoplastic composition.

[0078]

When a film excellent in transparency, moldability and resistance to whitening is needed, it is preferred to use such a material in which the free polymer (a-1), the core-shell block copolymer (a-2) and the block copolymer (b) consist of n-butylacrylate and methyl methacrylate, (a-1) has the glass transition temperature of is 60-80°C, proportions of core and shell in (a-2) are 60 % by weight of core and 40 % by weight of shell on the based of

the total weight of (a-2), proportions of (a-1) and (a-2) in the copolymer (a) are 50 % by weight of (a-1) and 50 % by weight of (a-2) on the base of the total weight of (a), proportions of methacrylic polymer block (A) and acrylic polymer block (B) in the block body (b) are 60 % by weight of (A) and 40 % by weight of (B) on the base of the total weight of (b), proportions of the copolymer (a) and the block copolymer (b) are 20% by weight of (a) and 80 % by weight of (b) on the base of the total weight of thermoplastic composition.

[0079]

[Example]

This invention will be explained in details by examples which do not limit this invention.

[0080]

BA denotes butyl acrylate and MMA denotes methyl methacrylate.

[0081]

Preparation Example 1

(Preparation of MMA-BA type free polymer with MMA-BA type core-shell graft copolymer)

In a 8 liter volume reactor equipped with an agitator, a thermometer, a nitrogen gas introducing pipe, a monomer addition unit and a reflux condenser, 200 parts by weight of distilled water and 1.0 % by weight of sodium dioctylsulfosuccinate as an emulsifier were added and then 30 parts by weight of a monomer mixture containing 85 % by weight of butyl acrylates, 15 % by weight of methyl methacrylate and 0.1 % by weight of triallyl isocyanurate as a cross-linking monomer was introduced into the reactor together with cumene hydroperoxide (0.1 % by weight in the monomer mixture) dissolve beforehand. Polymerization temperature is set at 40°C under stirring in nitrogen current. A solution of sodiumformaldehyde sulfoxylate (0.1 % by weight in the monomer mixture) dissolved in water was added gradually, and then polymerization was started. Polymerization was completed after an addition rate became higher than 95% in about 4 hours. The gel content of a bridged elastic emulsion obtained was 96.4%, the degree of swelling was 7.3 and the mean particle size of the emulsion was 1450Å.

Then, the polymerization temperature was elevated to 80°C, 20 parts by weight of a monomer mixture containing 50 % by weight of methyl methacrylate and 50 % by weight of butyl acrylate with a catalyst of cumene hydroperoxide (0.3 % by weight in the monomer mixture) was dissolved in the first monomer mixture. Beforehand, a solution of sodiumformaldehyde sulfoxylate (0.2 % by weight in the monomer mixture) dissolved in a small amount of water was introduced in the reactor a priori. Then, the monomer mixture was introduced by a pump under nitrogen current with stirring for about 2 hours to obtain (a-2-1). Then, in the presence of (a-2-1), the polymerization was continued by introducing 50 parts by weight of a monomer mixture of 80 % by weight of methyl methacrylate and 20 % by weight of butyl acrylate with a catalyst of cumene hydroperoxide (0.3 % by weight in the monomer mixture) by a pump for about 4 hours to effect polymerization of (a-1-1). The resulting polymer solution was changed to a salt with calcium chloride solution, rinsed and dried to obtain a dried powder copolymer (a-1).

(Gel content of cross-linked elastomer)

Cross-linked elastomer was placed in a 100-mesh wire netting, immersed in methyl ethyl ketone for 48 hours, then methyl ethyl ketone was eliminated under reduced pressure, the gel content was calculated by the following formula:

$$\text{Gel content} = (a) \times 100 / (b)$$

(a) : a weight after re-desiccation

(b) : a weight of a sample collected

(Glass transition temperature)

T_g was determined by the formula of Fox using the values (MMA; 105°C, BA; -54°C) described in "Polymer Hand Book, J. Brandrup, Interscience, 1989".

[0082]

Preparation Example 2

(Preparation of MMA-BA type block copolymer)

MMA-BA-MMA type block copolymer was prepared by following procedure. A 500 ml separable flask type polymerization reactor was purged with nitrogen. 1.25 g (8.7mmol) of copper bromides was weighed and 20ml of acetonitrile (desiccated by molecular sieves then bubbled with nitrogen) was added. After heating at 70°C under stirring for 5 minutes, cooled to room temperature again. Then, 0.63 g (1.7mmol) of initiator of 2,5-dibromo diethyl adipate and 89.4 g (100.0 ml) of butyl acrylate were added and 0.18 ml (0.9mmol) of ligand diethylenetriamine was added to start polymerization under heating at 80°C with stirring. The conversion of butyl acrylate was monitored in gas chromatograph by sampling about 0.2 ml of polymerization solutions at predetermined every time. Polymerization speed was controlled by adding triamine. When the conversion of butyl acrylate became 95%, 38.4 g (41.0 ml) of methyl methacrylate, 0.86 g (8.7mmol) of copper chlorides, 0.18 ml (0.9mmol) of diethylenetriamine and 123.1 ml of toluene (desiccation by molecular sieves followed by nitrogen bubbling) were added. The conversion of methyl methacrylate was determined by the similar method. When the conversion of methyl methacrylate became 85% and the conversion of butyl acrylate became 98%, 150 ml of toluene was added, the reactor was cooled with a water bath to terminate the reaction. The polymerization solution was always green during the reaction.

[0083]

The copper complex was removed by filtering the reaction solution through activated alumina. The obtained filtrate was added to a lot of methanol, the polymer was settled to obtain a target block copolymer (b-1) after vacuum drying at 60°C for 24 hours. The obtained block copolymer had a number average molecular weight M_n of 115000 by GPC analysis and a molecular weight distribution M_w/M_n of 1.50. A ratio of butyl acrylate/methyl methacrylate = 72/28 (wt%) by NMR.

(A molecular weight and molecular weight distribution)

GPC was measured by using a polystyrene gel column with chloroform as mobile phase to calculate a molecular weight of in term of polystyrene.

(Blocking ratio)

Soluble matters and insoluble matters are separated with ethanol and soluble matters were removed as homo polybutylacrylate. Then, soluble matters and insoluble

matters are separated by using a mixed solutions of 15/85 by weight of chloroform/ethanol and insoluble matter was removed as homo polymethylmethacrylate. Remained soluble fraction was the block copolymer and the blocking ratio (by weight) was calculated. proportions (weight ratios) of polybutyl acrylate and methyl polymethacrylate in the block copolymer were determined by $^1\text{H-NMR}$.

(Glass-transition temperature)

T_g was determined by using DSC (differential scanning calorimetry) according to JIS K7121 at a heating rate of 20°C/min.

Measurement in Examples and Comparative examples and evaluation were performed using following conditions and method.

[0084]

(Tensile strength)

Tensile strength was determined by the method of JIS K6251 at 0°C, n= 3 and an average value was adopted.

[0085]

(Whitening-resistance)

Whitening-resistance was evaluated on sample at broken part after the tensile test according to the above-mentioned test method.

(Transparency)

Transparency was measured for 50-micrometer-thick film at 23°C by hazemeter by Nippon Denshoku Industries Co., Ltd. to obtain the total light transmittance (TT) and Haze value (Hayes) (unit %).

[0086]

Example 1

33 parts by weight of a block copolymer: MMA-BA type block copolymer (b-1), 67 parts by weight of a copolymer (a-1) consisting of a free polymer and a core-shell type graft copolymer, and 0.2 parts by weight of Iruganox 1010 (Novartis International AG) as stabilizer were kneaded on a roll for 5 minutes at a temperature of 200°C. The resulting kneaded material was heat-pressed at a temperature of 200°C to obtain a flexible and transparent sheet of 2 mm thick. The obtained sheet showed an elastic modulus of 257MPa, a breaking strength of 20MPa and an elongation after fracture of 83%. No whitening mark was observed in the fracture surface after tensile test. Transparency measured on the sheet of 2 mm thickness which was heat-pressed at 200°C into a film of 250 micrometer thick was 93% (TT) and Hayes of 4%.

[0087]

Example 2

67 parts by weight of the block copolymer: MMA-BA type block copolymer (b-1), 33 parts by weight of the copolymer (a-1) consisting of a free polymer and a core-shell type graft copolymer, and 0.2 parts by weight of Iruganox 1010 (Novartis International AG) as stabilizer were kneaded on a roll for 5 minutes at a temperature of 200°C. The resulting kneaded material was heat-pressed at a temperature of 200°C to obtain a flexible and transparent sheet of 2 mm thick. The obtained sheet showed an elastic modulus of 6.4MPa, a breaking strength of 13MPa and an elongation after fracture of 167%. No

whithening mark was observed in the fracture surface after tensile test.

[0088]

Transparency measured on the sheet of 2 mm thickness which was heat-pressed at 200°C into a film of 184 micrometer thick was 93% (TT) and Hayes of 9%.

[0089]

Comparative Example 1

A sheet was produced by the same method as Example 1, except no block copolymer in Example 1 was added.

A sheet obtained was a transparent sheet. An elastic modulus was 688MPa, a breaking strength of 29MPa and an elongation after fracture of 33% but whithening was observed in the fracture surface after tensile test.

[0090]

Transparency measured on the sheet of 2 mm thickness which was heat-pressed at 200°C into a film of 244 micrometer thick was 93% (TT) and Hayes of 4%.

Comparative Example 2

A sheet was produced by the same method as Example 1, except no graft copolymer in Example 1 was added.

A sheet obtained was a rubber-like sheet with a feeling of a tuck. An elastic modulus was 0.8MPa, a breaking strength of 12MPa and an elongation after fracture of 423% and no whithening was observed in the fracture surface after tensile test. The sheet was heat-pressed at 200°C into a film but filing was difficult because of rubber-like nature.

[0091]

[Advantages of Invention]

Results of Examples 1, 2 and of Comparative Examples 1, 2 reveal that the film or sheet of prepared from a thermoplastic composition according to this invention possess excellent pliability, no whitening by bending and tension, and posses transparent property also.